MSc PROJECT REPORT ON

SYNTHESIS AND CHARACTERIZATION OF YBCO+SnO_2 COMPOSITE

SUBMITTED

BY

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CERTIFICATE

This is to certify that the project report entitled "**Synthesis and Characterization of YBCO+SnO_2 Composite**" submitted by **Ms Anannya Dutta** in partial fulfilment of the requirement towards the award of Master of Science degree in Physics at **National Institute of Technology, Rourkela**. This is an authentic work carried out by her under my supervision and guidance in low temperature laboratory of the Department of Physics and Astronomy. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institution.

Prof. D. Behera
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On the submission of my thesis report titled as "**Synthesis and characterization of YBCO+SnO_2 Composite**", I express my deep gratitude and appreciation to my guide **Prof D**. **Behera,** for his guidance and helpful discussion during the course of my work.

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ABSTRACT

In this paper pure YBCO is synthesized by solid state reaction method and measurement of resistivity versus temperature are taken by four probe method. YBCO is a high temperature superconducting material having transition above the liquid nitrogen temperature. SnO_2 was added to YBCO to form a composite in order to increase its current density and observe the changes in its properties. Microstructural analysis is performed using SEM, and phase confirmation of YBCO composite is done using X-Ray Diffraction method.DC electrical transport properties provide some understanding of the mechanism of this material. Now a days, research is going on to find mechanism of high temperature superconductivity as BCS theory is silent about this.

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CHAPTER 1

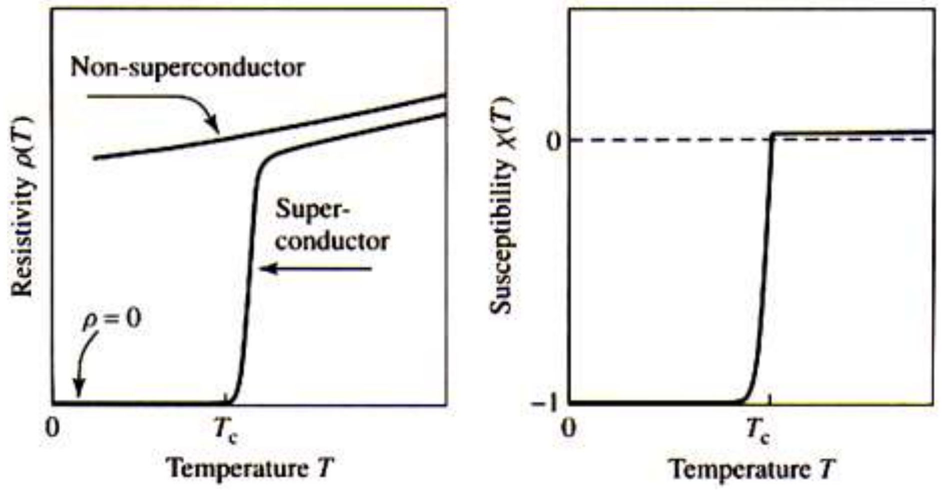
1. Introduction

1.1 General Remarks

The most unusual and interesting properties of solid is superconductivity in which the electrical resistivity falls suddenly to zero when the solid is cooled to a suitably low temperature and the specimen behave as perfect diamagnetic. The materials which obey both electrical ($\rho = 0$) and magnetic properties (-ve susceptibility) are called superconductors.Above the critical temperature a given specimen is in normal state and below the critical temperature it is in superconducting state. The two main characteristics of a superconductor are

i) Zero resistivity below critical temperature

ii) Negative susceptibility i.e.$\chi = -1$. It behaves as a perfect diamagnet.



(a) (b)

Figure.1. Superconducting phase transition

(a) zero resistivity at critical temperature **(b) negative susceptibility below critical temperature**

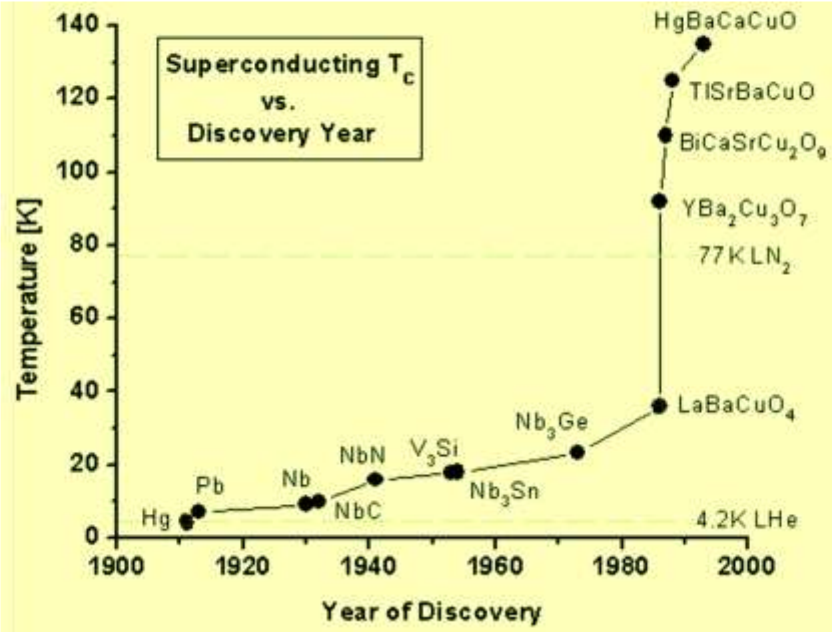


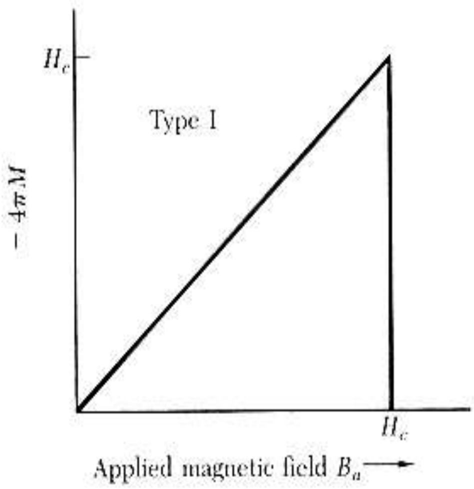
Figure. 2. Chronological development of superconductors

1.2 Types of superconductor

Superconductors are classified as two types based on the response to magnetic field

i) Type I superconductor

ii) Type II superconductor



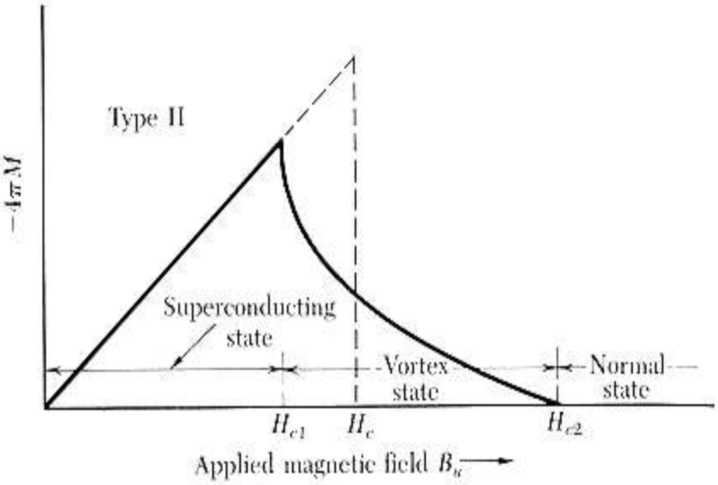


Fig. 3(a): Type 1 superconductor **Fig. 3(b) Type II superconductor**

Type I superconductor

- They strictly follow Meissner effect and exhibit perfect diamagnetism below the critical magnetic field. Above the critical field it behaves as a normal conductor.
- They are also well-known as **soft superconductors** because of the reason that they lose their superconductivity easily by application magnetic field.
- Examples are Aluminium (H_c = 0.0105 Tesla), Zinc (H_c = 0.0054)

Type II superconductor

- They follow Meissner effect to a certain extent. For $H<H_{c1}$, the material exhibits perfect diamagnetism no flux penetration occurs. Between H_{c1} and H_{c2} the flux begins to penetrate and at Hc_2, there is complete penetration and the material becomes a normal conductor. The region between H_{c1} and H_{c2} is called vortex or intermediate region.
- They are also known as **hard superconductors** because they can bear magnetic field to an appreciable extend.

1.3 HIGH TEMPERATURE SUPERCONDUCTOR (HTSC)

HTSC have a superconducting transition temperature above 30K or 77 K i.e above the boiling point of liquid nitrogen. Much higher magnetic field is needed to suppress superconductivity in these superconductors as they allow magnetic field to penetrate their interior in quantized units of flux. Critical temp as high as 135K have been achieved in HBCCO system. Examples of HTSC are LBCO, YBCO, LSCO, BSSCO, TBCCO, and HBCCO.

Table 1 Critical temperatures of various HTSCs

HTSC	T_C
YBCO	92K
LSCO	108K
BSCCO	110K
TBCCO	127K
HBCCO	135K

There is always a demand for materials having superconducting properties as superconductivity has applications in many fields such as electrical power transmission, high speed trains, large physics machines, optoelectronics magnetic levitation, magnetic shielding etc. They are also less expensive and better than the former one. The major challenge now-a-days is to synthesize a superconducting material whose critical temperature is close to room temperature. Heading towards this path the current focus of much of the research, development and commercialization of superconductors is on $YBa_2Cu_3O_{7-\delta}$.

1.5 Properties of superconductors

The physical properties of superconductors vary from material to material. It depends on their critical temperatures and the critical field applied.

1.5.1 Meissner effect:

When a weak magnetic field is applied to a superconductor, it expels all the flux completely. This is called Meissner effect. It was developed in 1913.The superconductivity is destroyed when the magnetic field is gradually increased beyond H_c.

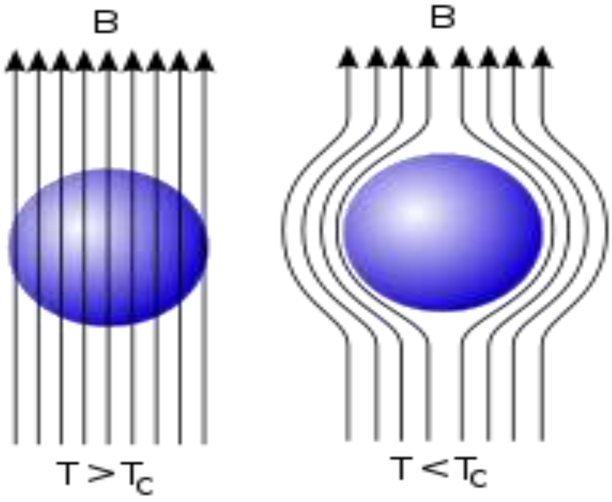


Fig.4 Meissner effect

1.5.2 Zero electrical resistance

When a superconductor is cooled below a certain temperature i.e the critical temperature its resistivity falls to zero. This is the property of a superconductor and above this temperature these material show normal metallic behaviour.

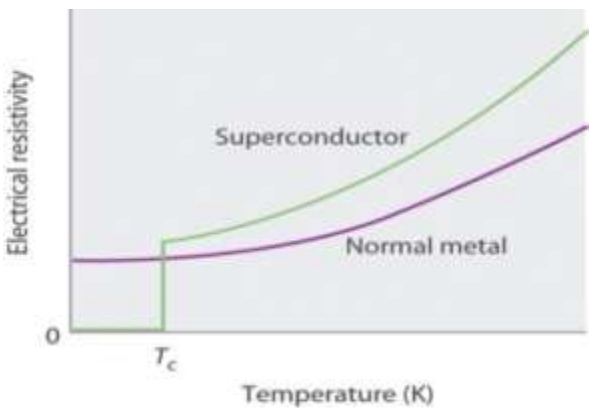


Figure-5 (electrical resistivity vs temperature)

1.5.3 Isotope effect:

The transition temperature of a sc material varies with their average isotopic mass, M, of their constituents as,

$$T_c \propto M^{-\frac{1}{2}}$$

1.5.4 Specific Heat:

The specific heat of superconductors shows a transition at T_c since superconductivity affects electrons mainly so lattice vibration part remains unaffected and we find that the electronic specific heat is nonlinear with temperature.

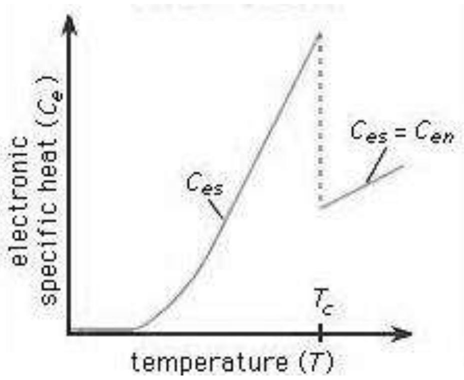


Figure. 6. Variation of specific heat with temperature

1.5.5 Effect of magnetic field:

The magnetic induction inside a specimen is given by

$$B = \mu_0(H + M)$$

Where H is the external magnetic field and M is the magnetization. According to Meissner effect there is zero magnetic induction inside the superconductor. $\mu_0(H + M) = 0$

$$\text{Or,} \quad M = -H$$

Such a material is perfectly diamagnetic with susceptibility $\chi = -1$

CHAPTER 2

2.1 $YBa_2Cu_3O_{7-\delta}$(YBCO) High temperature superconductor:

Yttrium Barium Copper Oxide, often abbreviated as YBCO, is a crystalline solid with the formula $YBa_2Cu_3O_{7-\delta}$. It is a famous high-temperature superconductor, as it was the first material to achieve high transition temperature above 77 K. It is a black solid whose molar mass is 666.19 and density is 6.3gm/cm^3. It is insoluble in water. The superconducting properties are sensitive to the value of (δ), its oxygen content. Here conduction mostly occurs in the planes containing the copper oxide. It has been found that the critical temp is very sensitive to the average number of oxygen atoms present which can vary. For this reason the formula for 1-2-3 SC is given by $YBa_2Cu_30_{7-\delta}$ where δ is a number between 0 to 1. Only those materials with $0 \ll \delta \ll 0.65$ are superconducting below T_c, and when x=0.07 the material superconducts at the highest of 92K.

<u>Structure of HTSC</u>:

High temperature superconductors (HTSCs) are structurally members of a crystallographic family known as perovskites.

Perovskite Structure

Perovskites are ceramics which is a combination of metallic elements and non-metals, usually oxygen that have a particular atomic arrangement. They have their generalised formula as ABX_3. The A and B atoms are metallic cations and X atoms are non-metallic anions.

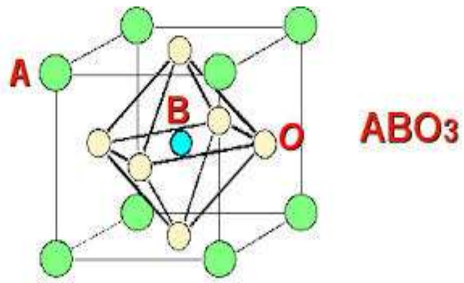


Fig.7 Perovskite structure

Structure of YBCO:

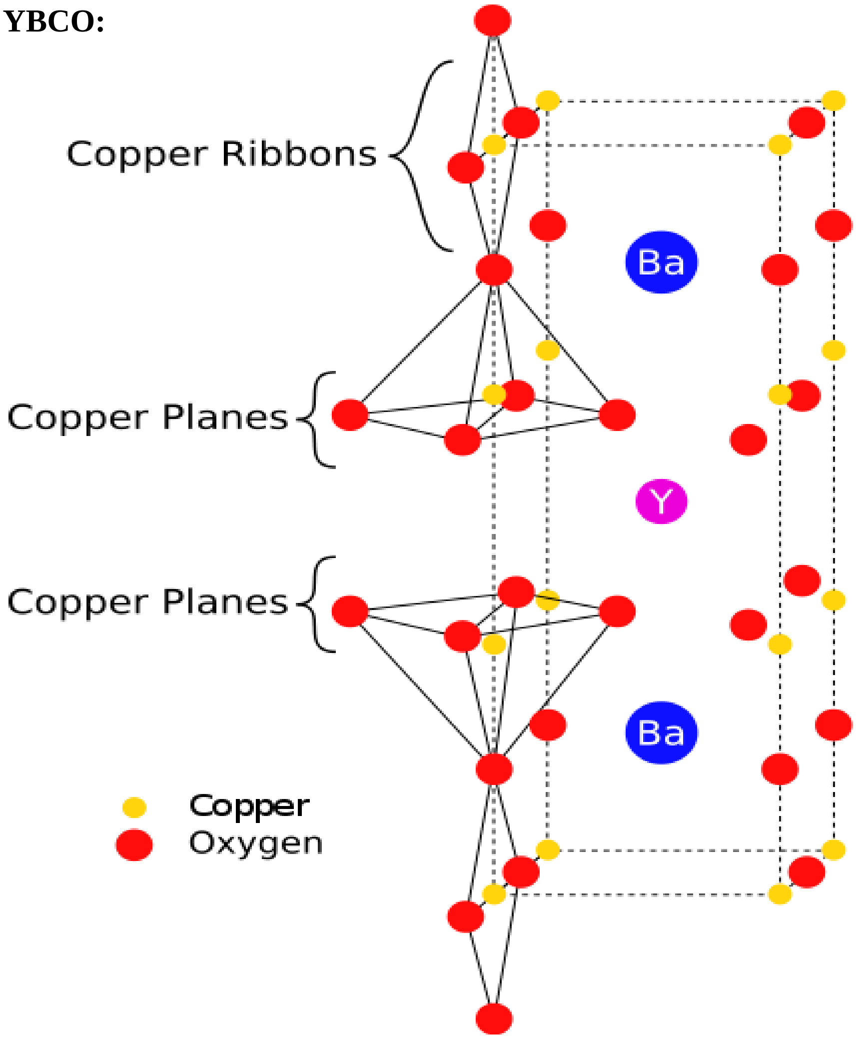


Fig 8 : Structure of YBCO

The compound $YBa_2Cu_3O_7$ has orthorhombic symmetry. The structure can be described as a perovskite with an shortage of oxygen. By eliminating oxygen atoms from the ideal perovskite lattice, we can obtain $YBa_2Cu_3O_7$.

Its unit cell contains.

– A layer of Cu–O having copper is surrounded by four oxygen ions

– A layer of BaO

– A layer of Cu–O, where Cu is surrounded by five oxygen ions forming a polyhedron

– A layer of yttrium shortage of four oxygen.

Thus, the stacking sequence of the (*ab*) planes is Y–CuO–BaO–CuO2–BaO–CuO2–Y. It is to be noted that there are Cu–O chains along the *b*-axis. The presences of oxygen atoms in these chains are essential for superconductivity. The general formula of the compound is $YBa_2Cu_3O_{7-x}$ where $0 \leq x \leq 1$.The lattice parameters vary with the oxygen content (x-value) and for $x \geq 0.6$the structure is tetragonal. In $YBa_2Cu_3O_6$(x = 1), there are no chain (O4sites) oxygen and Cu in b-axis is in the 1^+state. (Non-superconducting state).Thus, the unit cell parameters vary with the value of x in $YBa_2Cu_3O_{7-x}$ (i.e. a, b and c parameters vary with the oxygen-stoichiometry). The structure is orthorhombic for x = 0.

<u>SnO_2:</u>

Tin oxide, also known as stannic oxide is an inorganic compound with molecular formula SnO2. It is a colourless, white to off white coloured powder. Its mineral form is a main ore of tin. It is diamagnetic and amphoteric in nature. It is a crystalline solid having rutile structure.

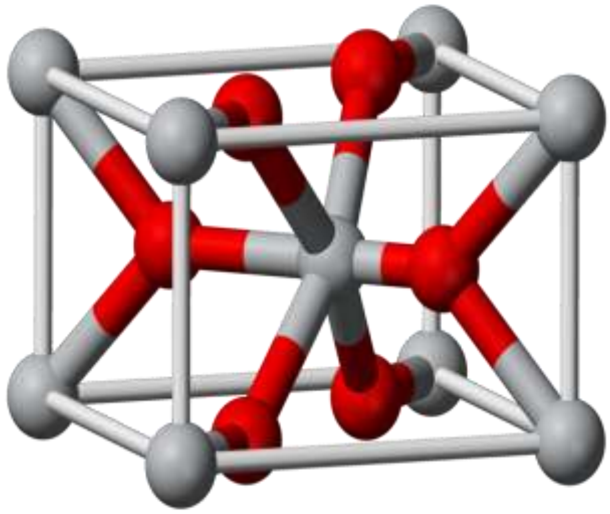


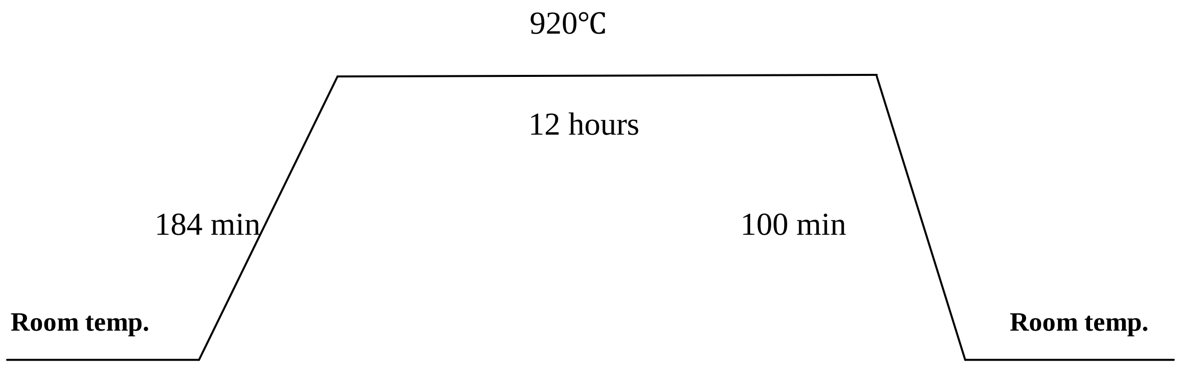
Figure 9: Structure of Tin oxide

CHAPTER 3

SAMPLE PREPARATION

Heating profile:

(a) <u>Heating profile for calcinations:</u>



High temperature superconductors are prepared using the Solid state reaction method. The steps involved are:

1. Assimilation the powders
2. Calcinations with intermediary grinding
3. Annealing in the presence of oxygen at 500 ^{0}C for 8 hours.

This reaction takes place at high temperature. After the reaction has taken place, theYBCO should be reground to a powder and then pressed into a pellet.

YBCO was prepared by mixing the chemicals as per the balanced chemical equation.

$$\frac{1}{2}Y_2O_3 + 2BaCO_3 + 3CuO + \frac{1}{2}O_2 \rightarrow YBa_2Cu_3O_7 + \ 2CO_2$$

Steps involved in the preparation of YBCO are as follows:

1. Yttrium oxides (Y_2O_3), Barium Carbonate ($BaCo_3$), Copper Oxide (CuO) were taken in stoichiometric ratio (1:2:3) to prepare $YBa_2Cu_3O_{7-\delta}$.
2. The precursor powders are mixed together in an agate mortar for 2-3 hours to get the gray powder of YBCO.

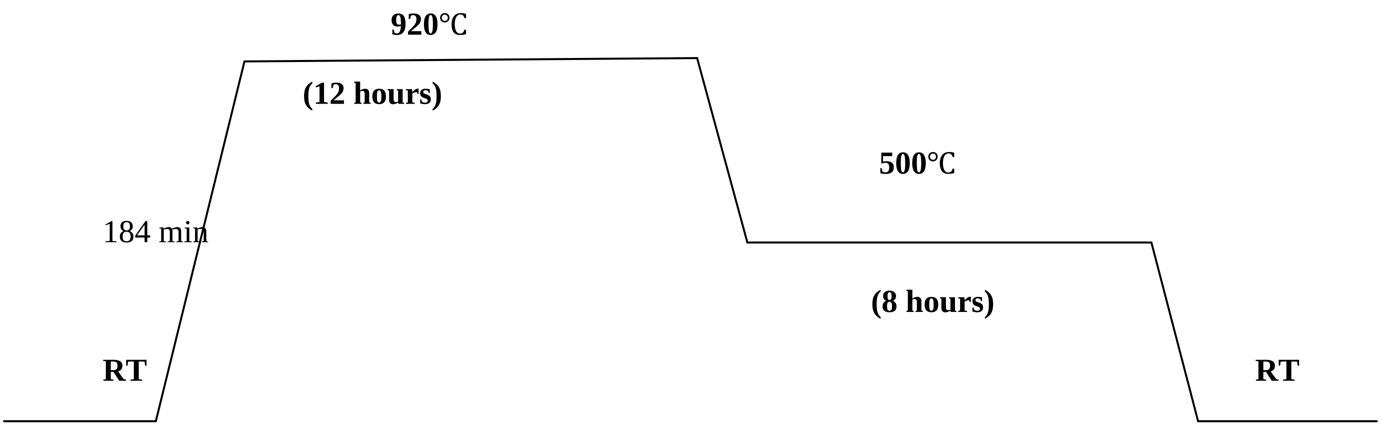
3. The grounded sample was taken in an alumina crucible and subjected to calcinations (which promotes the decomposition of carbonates, nitrates or any other impurity phase leading to the formation of desired phase of the superconducting YBCO) at 900℃ for 12 hours for 5 times followed by intermediate grinding.
4. The mixture was taken out after the desired temperature was reached.
5. The calcined powder so obtained was ground well and pressed in the form of pellets using a pelletizer giving a pressure of 100kg/m^2.
6. The YBCO pellets were sintered in an indigenous programmable conventional furnace at 920℃ for 12 hours annealed at 500℃ for 8 hours in oxygen atmosphere.

Preparation of composite of YBCO with SnO_2:

SnO_2 powder was added to pristine superconducting YBCO powder in various wt.%. The different composites were ground individually for one hour. Each composition was pressed into pellets and was sintered at920℃ for 12 hours and anneled at 500℃ for 8 hours in oxygen atmosphere and allowed to cool slowly within the furnace to room temperature.

The different wt. % of SnO_2 added to YBCO are x= 0.0, 0.01, 0.05, 0.1wt. %.

(a) Heating profile for sintering:



CHAPTER 4

CHARACTERIZATION TECHNIQUES

4.1 X-RAY DIFFRACTION (XRD)

X-rays are produced generally by either x-ray tubes or synchrotron radiation. Waves are diffracted from different atoms. If the atoms are arranged in a periodic way the diffracted waves consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern allow us to figure out the distribution of atoms in a material. This is governed by Bragg's Law given by,

$$2dSin\theta = n\lambda$$

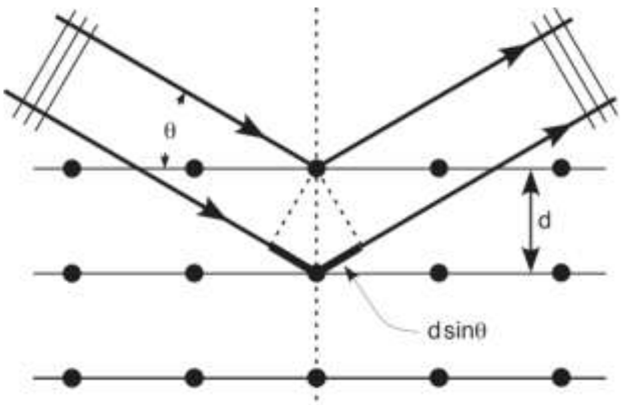


Figure 10: Diffraction through crystal planes

4.2 SCANNING ELECTRON MICROSCOPE (SEM)

SEM is used to know the external morphology and chemical composition of the sample. It uses electrons instead of light to scan an image. It can scan an image very fast and also over a large area. It is also followed by EDXS which analyzes the elements present in the sample and also quantify their amount.

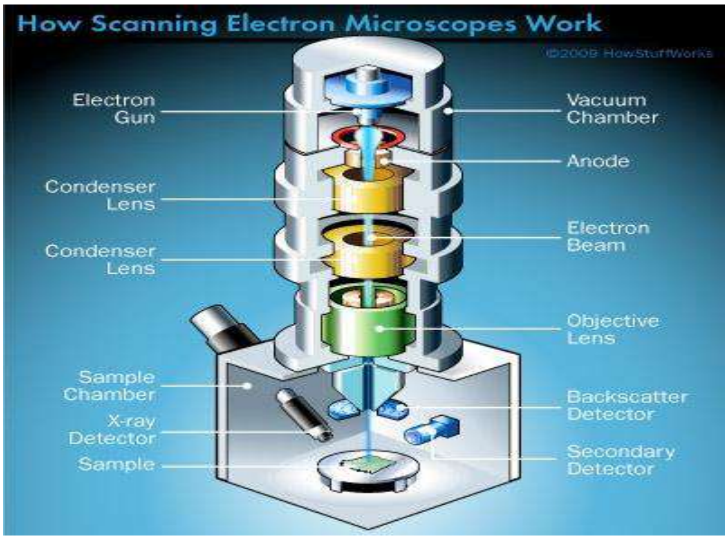


Figure 11: Schematic diagram of a SEM

4.3 LOW TEMPERATURE R-T MEASURMENT BY FOUR PROBE METHOD:

The temperature dependence of resistivity was measured using four probe method. Two probe method is not used due to some of its demerits.

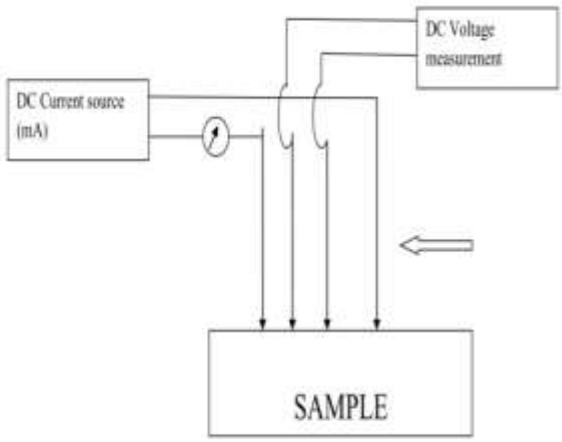


Figure 12: Four probe set up for resistance measurement

CHAPTER 5

5. Result and discussion

5.1 *Structural analysis by XRD*:

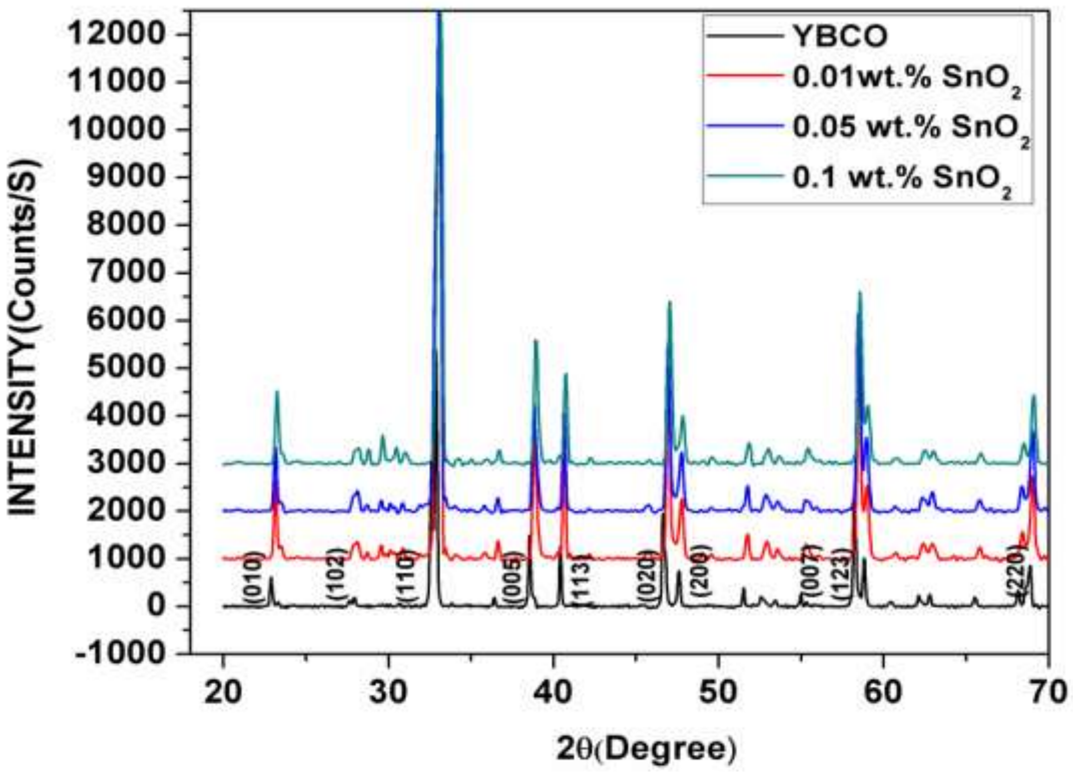


Fig 13: XRD graph of YBCO+xSnO_2 (x= 0.0, 0.01,0.05,0.1 wt. %) composites.

Figure 11 shows the XRD pattern of YBCO+ xSnO_2 (x=0.0, 0.01, 0.05, 0.1 wt. %) composites. Indexing of the pattern shows that all the samples are in orthorhombic structure with space group P_{mmm}. Some SnO_2 peaks are also seen in the pattern. It is also observed that the structure has not changed even after doping SnO_2. The symmetry has also not changed after doping. It concludes that the addition of SnO_2 to pure YBCO has no significant effect on the structure and symmetry of the composites. The lattice parameters and unit cell volumes calculated by check cell software are listed in Table2 below.

Table 2. Lattice parameters calculated from XRD graphs

SnO_2(wt.%)	a (A^0)	b (A^0)	c (A^0)	V (A^{03})
YBCO	3.818 (1)	3.884 (1)	11.681 (2)	173.218
0.01	3.818 (1)	3.873 (1)	11.630 (4)	171.974
0.05	3.817 (1)	3.871 (1)	11.647 (4)	172.091
0.1	3.795 (1)	3.898 (1)	11.711 (5)	173.239

The lattice parameters changes with the addition of SnO2.Here we see that the volume decreases as we decrease the doping concentration. The highest concentration added has nearly same volume as that of pure YBCO.

5.2 *Scanning electron microscopy (SEM):*

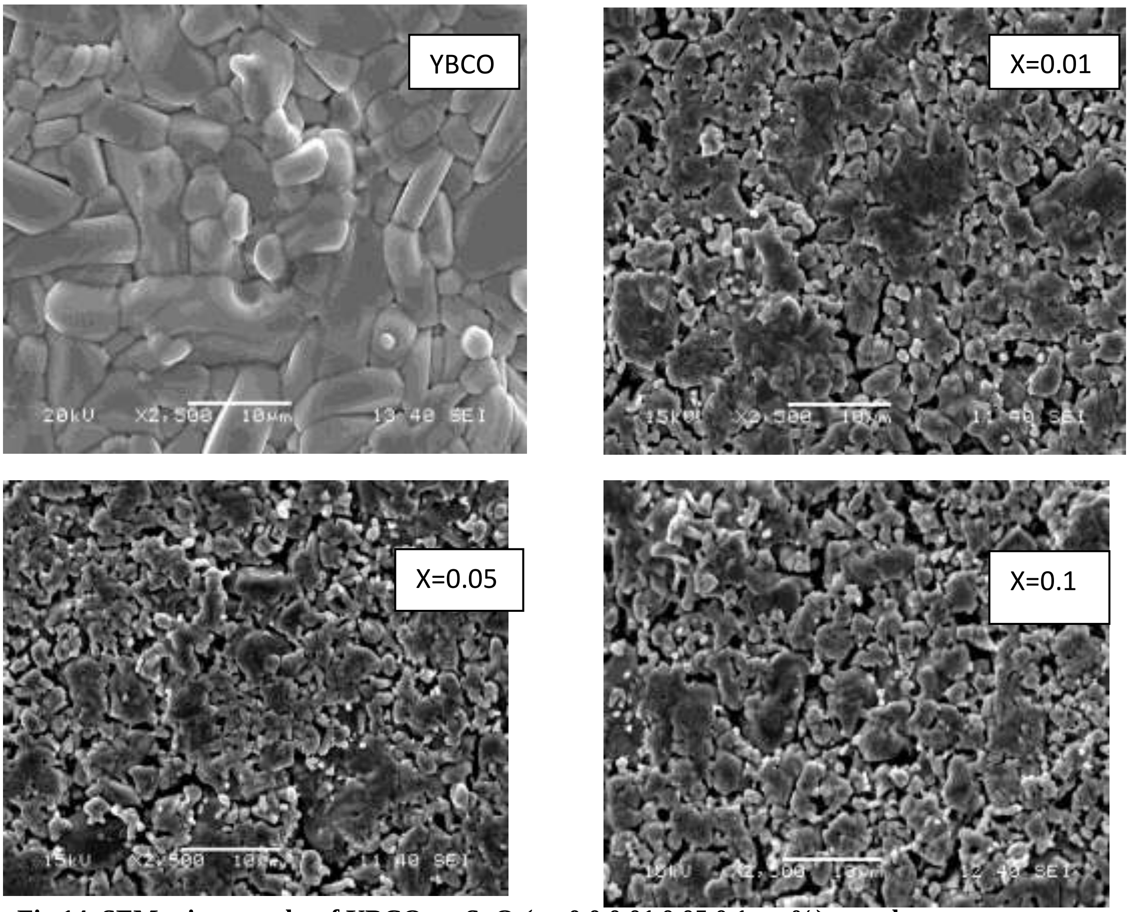
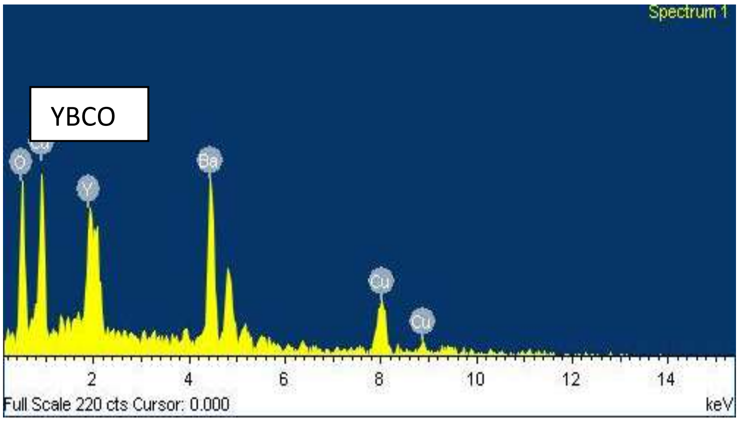


Fig.14. SEM micrographs of YBCO+ x SnO_2(x= 0.0,0.01,0.05,0.1 wt.%) samples.

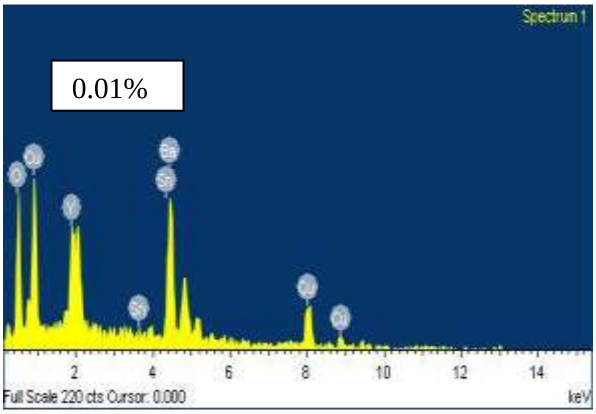
It shows that pure YBCO has long and extended grains randomly oriented in all direction with size varying from 1 to 10µm. Grains are very closely packed to each other. With the addition of SnO_2 the grain size decreases to a large extent with the increase of pores and voids in the sample. The grains become rounder in shape.

5.3 EDX analysis:

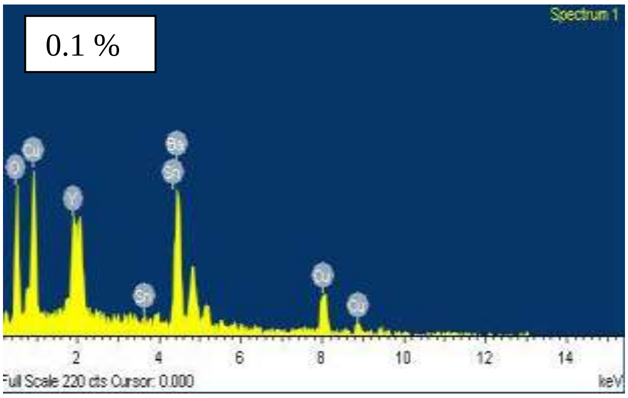
The elemental analysis and their percentage composition was confirmed by EDXA. The presence of the elements Yttrium, Copper, Barium, and Oxygen was observed by the peaks of EDXA. The presence of Tin was also confirmed by EDX image after doping. The weight % and atomic % composition is given in the tables below.



Element	Weight%	Atomic %
O	12.84	46.78
Cu	28.70	26.33
Y	9.03	5.92
Ba	49.43	20.97



Element	Weight %	Atomic %
O	14.10	49.18
Cu	29.82	26.20
Y	7.89	4.95
Sn	1.14	0.54
Ba	47.05	19.13



Element	Weight%	Atomic %
O	14.98	51.08
Cu	27.95	23.99
Y	9.91	6.08
Sn	1.87	0.86
Ba	45.29	17.99

Fig. 15. EDX picture of YBCO+x SnO_2(x= 0.0, 0.01, 0.1 wt.%) samples.

5.4 *Temperature vs Resistivity Measurement*

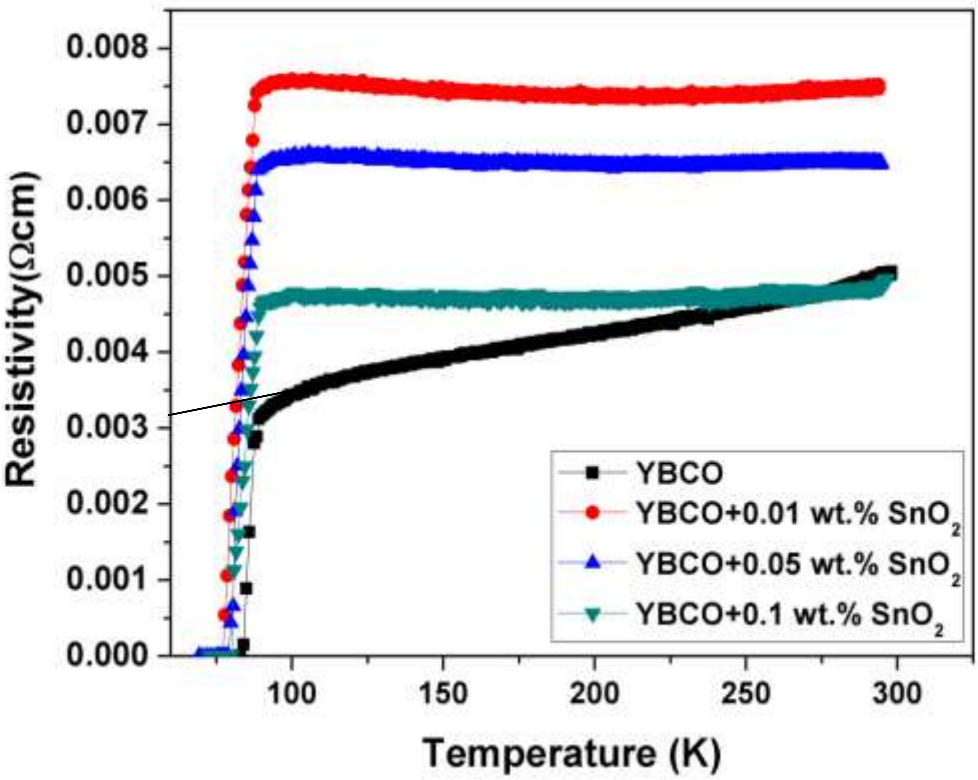


Fig.16 Temperature vs. Resistivity plots forYBCO+xSnO_2 (x=0.0, 0.01, 0.05, 0.1wt. %) samples.

Measurement of the resistivity dependence of temperature for different samples with various amounts of SnO_2 is shown in Fig.17.Pure YBCO shows metallic behaviour. But with the addition of SnO_2 the metallic behaviour decreases with the increase in concentration of SnO_2.

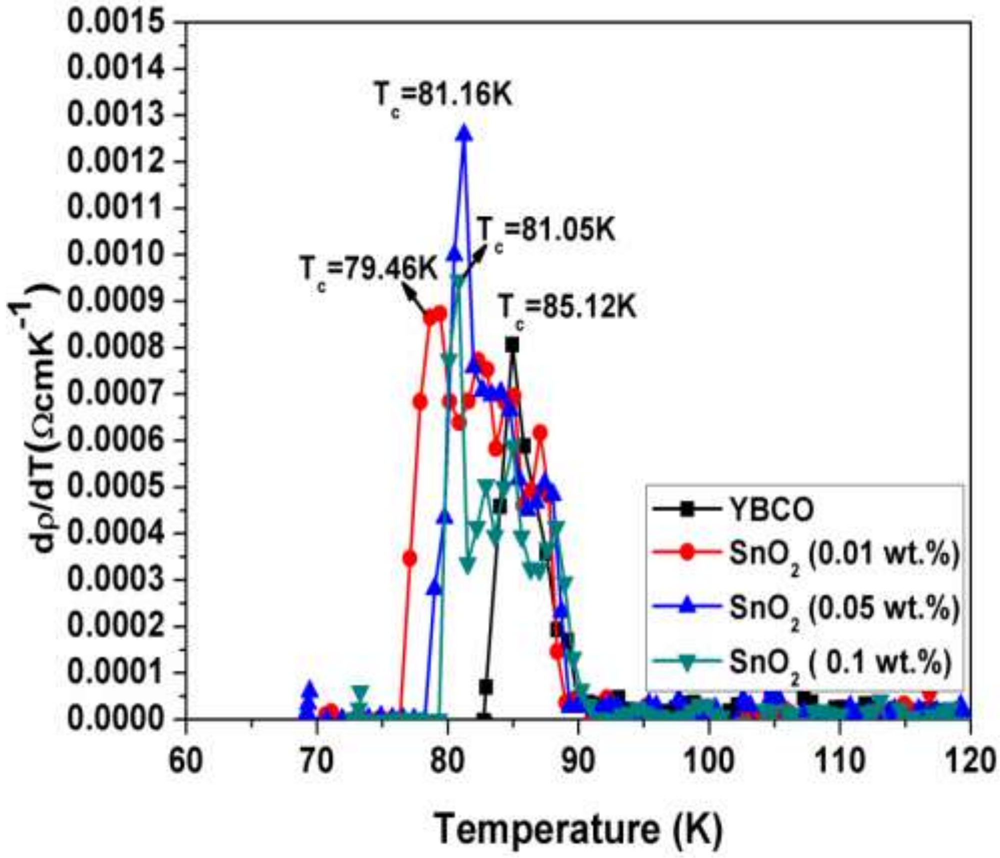


Fig.17. Temperature derivative of Resistivity plots for YBCO+xSnO_2 (x=0.0, 0.01, 0.05, 0.1wt. %) samples.

There are two regions- the normal region and the superconducting region and in this region it follows Anderson and Zou relation given by$\rho_r(T) = a + bT$where a is the intercept gives the residual resistivity ρ_0 and b is the slope and then extrapolating to T_c gives the slope. Different critical temperatures are observed from the different composites. The derivative of the RT graph was done to get the critical temperatures. The temperature derivative of resistivity curves are shown in fig.18. T_c is defined as the peak position of the derivative and is observed to decrease with the addition of SnO_2.The peak broadening is occurring due to addition of SnO_2composite which is affecting the inter granular weak link between grains.

Table 3 Critical temperatures from R~T graph for YBCO+xSnO_2(x=0.0, 0.01, 0.05, 0.1 wt. %) samples

SnO_2 (wt.%)	T_{c0}(K)	T_c(K)
0.0	82.91	85.12
0.01	76.38	79.46
0.05	78.27	81.16
0.1	79.77	81.05

CHAPTER-5

CONCLUSION

High temperature superconductor YBCO was synthesized using solid state reaction method. The effect of addition of tin oxide (SnO_2) to YBCO was studied by various characterization techniques. The phase of YBCO was confirmed by XRD analysis and the critical temperature was found out to be 85.12K by RT measurements. Various critical temperatures are found for different compositions of SnO_2 in YBCO. The morphological analysis was done by Scanning electron microscope and the presence of SnO_2 was confirmed by EDX analysis. The grain boundaries decrease with the increase in concentration of SnO_2. Addition of the material to YBCO matrix decreases the transition temperature as resistance of the weak link Josephson junction increases.

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